Absorption of Nitrogen by Molten Iron Alloys. II : Study on Fe-Ni, Fe-Cr and Fe-Mn Alloys

Absorption of Nitrogen by Molten Iron Alloys. II
Study on Fe-Ni, Fe-Cr and Fe-Mn Alloys*

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Synopsis

The absorption phenomena of nitrogen by molten iron alloys (Fe-Cr, Fe-Mn and Fe-Ni binary alloys) were studied, and the experimental results were discussed from the view of the statistical thermodynamics under the same conception formerly reported.

I. Introduction

With the same purpose as explained in Part I[1], the solubility of nitrogen in iron alloys (in the whole range of Fe-Ni, Fe-Cr and Fe-Mn alloys) was studied.

The determination of solubility became difficult or impossible in the absorption experiment (i. e., the method I explained in Part I) when above a certain amount of chromium or manganese was alloyed, for vapourized chromium or manganese absorbed nitrogen gas intensely in its condensed state, and hence the normal saturation curves were not obtained. Such an inevitable phenomenon accompanied in the course of the method I made also the measurement of temperature inaccurate, but the volume of evolved gas during solidification could be measured as usual. Hence, in such a case the method II was mainly adopted for the determination of solubility.

II. Experimental Results

[A] Fe-Ni Alloys

Typical curves in which the absorbed values are plotted against time are shown in Fig. 1 and the solubility of nitrogen at about 1,600°C is plotted as a function of the nickel percentage in Fig. 2. From these curves it is found that the saturation value and absorption rate decrease with the increase of nickel percentage, and the alloys containing over 80% Ni hardly absorb nitrogen. As to the temperature coefficient of saturation value, the following results were found: the values

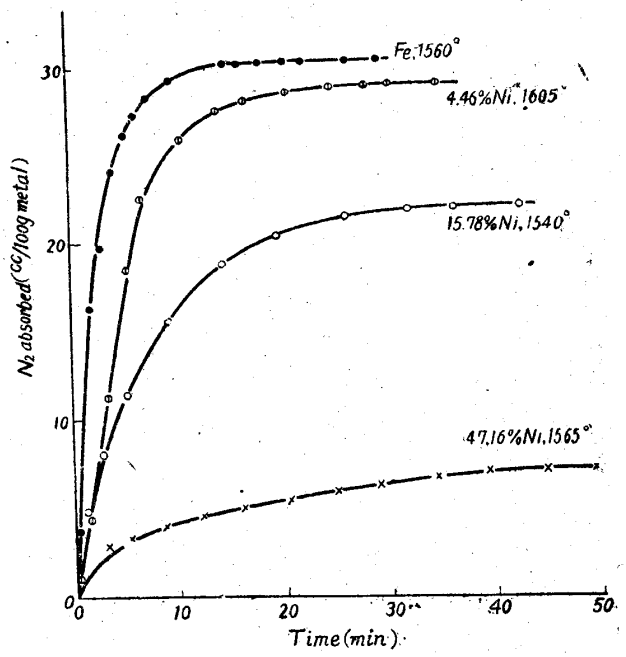

Fig. 1. Absorption of N_2 by Fe-Ni alloys.

of low-alloy irons do not differ appreciably from that of pure iron; in the nickel-side these values could not be measured accurately owing to the small absolute value of saturation; in all the alloys in this system, the value was positive, that is, the saturation value increased as temperature rose.

[B] Fe-Cr Alloys

Some examples obtained in the absorption experiments (method I) are shown in Fig. 3. From these curves, it is clear that the

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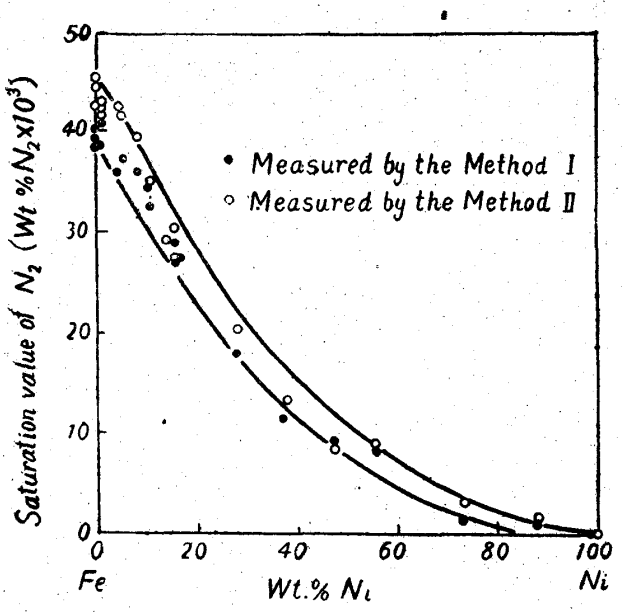

Fig. 2. Absorption values of N_2 by Fe-Ni alloys. (Relation between saturation value and Ni-content.)

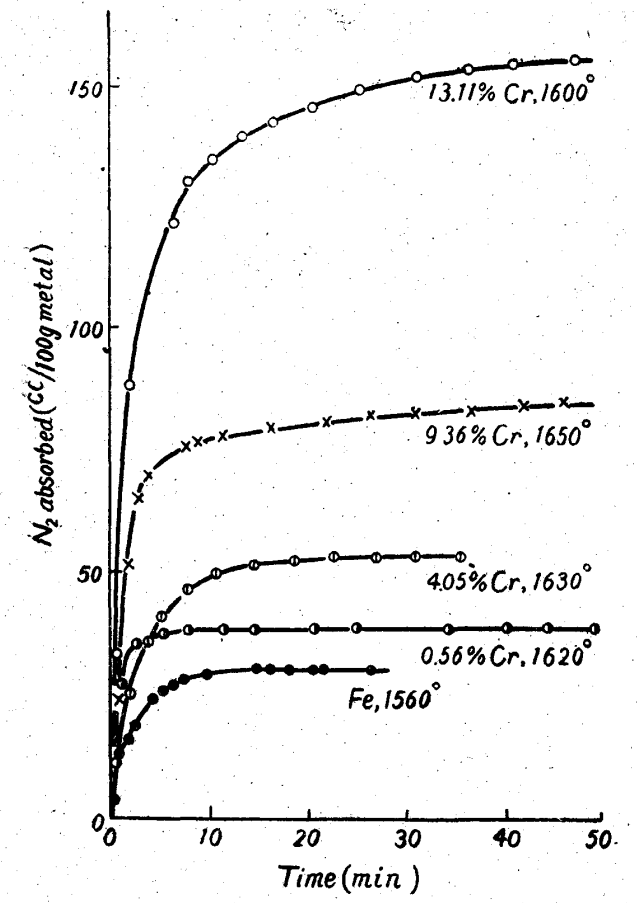

Fig. 3. Absorption of N_2 by Fe-Cr alloys.

determination of solubility by the method I is impossible over 10% Cr, owing to the appreciable absorption by vapourized and condensed chromium. Therefore, with respect to the alloys containing over 10% Cr, the saturation values were determined only by the method II.

The solubility of nitrogen in the alloys of this system has been measured by Brick and Creevy[2] by means of the method II, in which the content of nitrogen in the quenched sample was determined by the vacuum fusion method. In Fig. 4 the present data are

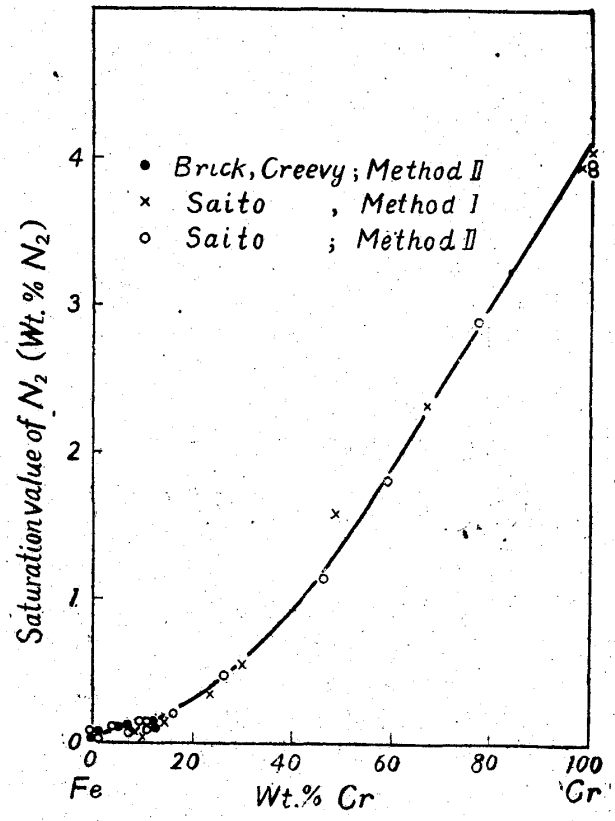

Fig. 4. Absorption values of N_2 by Fe-Cr alloys. (Relation between saturation value and Cr-content.)

shown together with those made by them. In both cases the experiments were performed over 100-150°C above the melting point. As shown in Fig. 4 the coincidence of the two inspires confidence in the results. Further, it was found in the course of the absorption experiments (method I) on the alloys containing over 5% Cr that the temperature coefficient of saturation value was negative, and the melting point was lowered by the absorption of nitrogen, but the author was compelled to give no accurate data owing mainly to the inaccurrcy of temperature measurement inevitably accompained by the vapourization of chromium.

[C] Fe-Mn Alloys

As shown in Fig. 5 the normal saturation curves could not be obtained by the method I even in the 1% Mn-alloy, because of the intense vapourization of manganese which

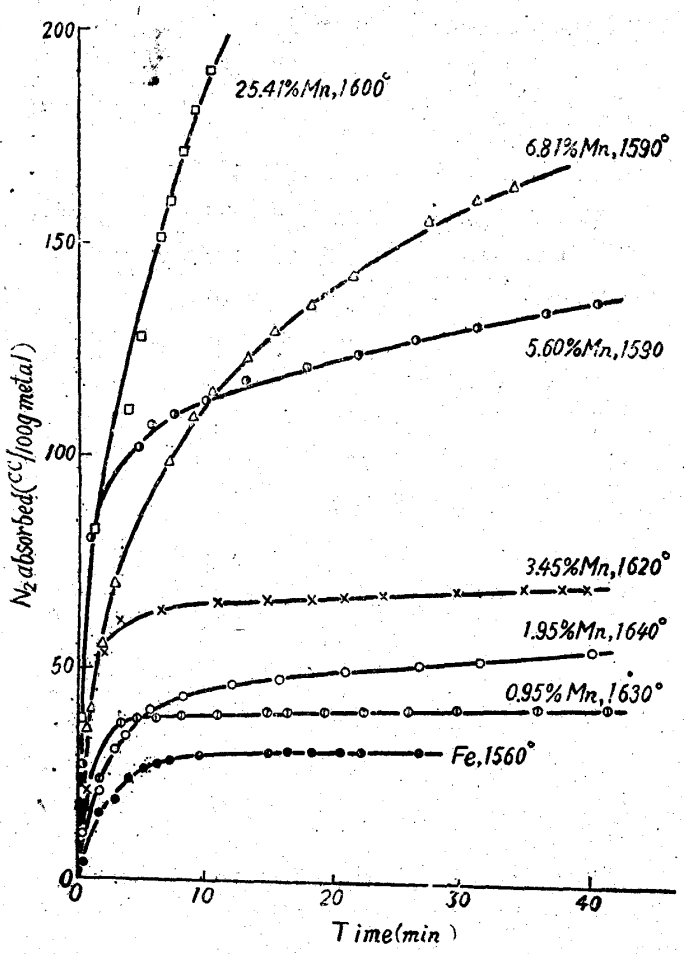

Fig. 5. Absorption of N_2 by Fe-Mn alloys.

was more pronounced than that of chromium above mentioned. The approximate values of saturation were estimated by this method I only in the alloys containing not more than 5% Mn. Hence, in the alloys of this system, experiments were carried out as follows: the sample (about 150 g) was melted by the induction furnace under the cover of slag $CaO{\cdot}Al_2O_3{\cdot}SiO_2$ to avoid the vapourization loss of manganese; it was saturated with nitrogen gas by streaming and bubbling it in the melt (the velocity of stream was about 200 cc/min.); then it was quenched in water and the nitrogen content was determined by the usual process. It was determined previously by the preliminary experiments that the time of bubbling necessary for the saturation was about 15 min. and the volume of evolved gas during solidification was negligibly small compared to its nitrogen content when the sample was quenched as above. The temperature was measured by means of Pt-Pt·Rh thermocouple, since the melting point of this system is not so high.

The results obtained are plotted in Fig. 6 in which the temperature of experiments was about 1,400°C in the Mn-side over 50% Mn and was 100–150°C above the melting point in the Fe-side. The temperature of experiment and melting time were restricted owing to the intense attack of slag on crucible.

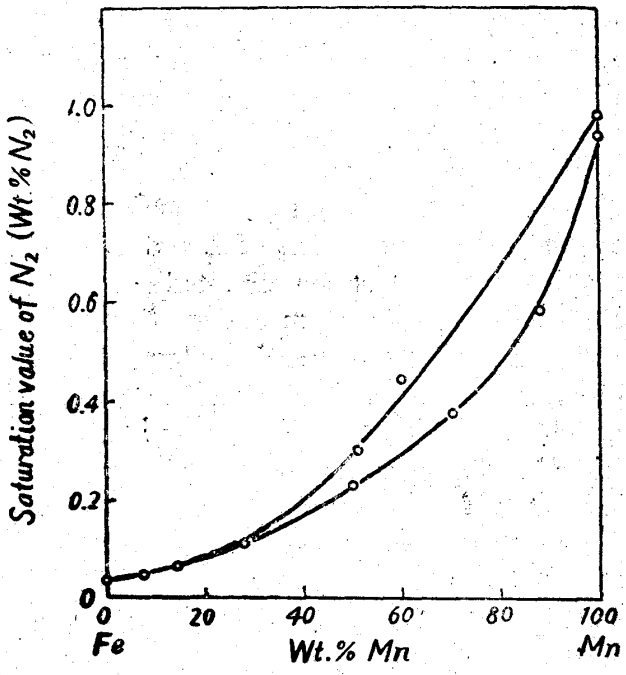

Fig. 6. Absorption values of N_2 by Fe-Mn alloys. (Relation between saturation value and Mn-content.)

III. Discussion

The experimental results on Fe-Ni, Fe-Cr and Fe-Mn alloys above mentioned will be interpreted on the same idea as the former report that the structure of melt is quasi-crystalline and the absorbed gas atoms are situated in molten metal lattice interstitially.

[A] Considerations on the Absorption of Nitrogen by Molten Iron Alloys from the View of Statistical Thermodynamics

When another element alloys with iron, the potential field in which absorbed nitrogen atoms exist changes from that of pure iron. Since the potential energy between atoms decreases rapidly as the distance between them increases, it may approximately be assumed that the absorbed nitrogen atoms exist in the potential field which is subjected to the effect only from the nearest neighbouring atoms.

Now, in the case of alloy which contains x-mole fraction of another atom A (hereafter this will briefly be called x-alloy), the statistical arrangement of atoms will prevail if there are no particular circumstances; that is, there are zx atoms of A and $z(1-x)$ atoms of Fe around a nitrogen atom absorbed; in other words, the distribution of atoms around a nitrogen atom absorbed corresponds to the mean concentration of the alloy. However, the interaction energy between a nitrogen atom and a metal atom differs from that between a nitrogen atom and another kind of metal atom as will be mentioned hereafter, so that it must be generally considered that $z\xi(x)$ atoms of A and $z[1-\xi(x)]$ atoms of Fe must be situated around an absorbed nitrogen atom, when $\xi(x)$ is the probability of existence of A-atom around a nitrogen atom and $0 \leqq \xi(x) \leqq 1$. Then, the potential field in the x-alloy in which absorbed nitrogen atoms exist and move should have the following form: $z\{\psi_F[1-\xi(x)]+\psi_A\xi(x)\} = \Psi_F - \xi(x)(\Psi_F - \Psi_A)$, where ψ_F is the interaction energy of the pair of nitrogen and iron atoms, and ψ_A that of nitrogen and A-atoms; $z\psi_F = \Psi_F$, $z\psi_A = \Psi_A$ following the notations adopted in the first report.

Thus, it can be treated in the same manner as the first report with the following results: The total partition function of nitrogen atoms absorbed in the x-alloy Γ_N^m:

$$\Gamma_N^m = \frac{N!}{n!(N-n)!}\left(\frac{T}{\theta}\right)^{3n} e^{-\frac{n[\Psi_F - \xi(x)(\Psi_F - \Psi_A)]}{kT}} (\varepsilon_N \rho_N)^n, \quad (1)^*$$

its free energy G_N^m:

$$G_N^m = -kT\log\Gamma_N^m = -kT[N\log N - n\log n - (N-n)\log(N-n)] - nkT\log\left(\frac{T}{\theta}\right)^3\varepsilon_N\rho_N + n[\Psi_F - \xi(x)(\Psi_F - \Psi_A)], \quad (2)$$

the chemical potential of nitrogen atom in the x-alloy μ_N^m:

$$\mu_N^m = \frac{\partial G_N^m}{\partial n} = -kT\log\left[\frac{(N-n)}{n}\left(\frac{T}{\theta}\right)^3\varepsilon_N\rho_N\right] + [\Psi_F - \xi(x)(\Psi_F - \Psi_A)], \quad (3)$$

and its absolute activity λ_N^m:

$$\lambda_N^m = \frac{n}{N-n}\left(\frac{\theta}{T}\right)^3(\varepsilon_N\rho_N)^{-1}e^{\frac{\Psi_F - \xi(x)(\Psi_F - \Psi_A)}{kT}}. \quad (4)$$

Equilibrium condition will be obtained by equating μ_N^m and μ_N^g, or λ_N^m and λ_N^g, and hence the absorption formula of x-alloy will be expressed in the following form:

$$\left(\frac{n}{N-n}\right)_x = \lambda_N^g\left(\frac{T}{\theta}\right)^3 e^{-\frac{[(\Psi_F + \frac{\chi_d}{2}) - \xi(x)(\Psi_F - \Psi_A)]}{kT}}\varepsilon_N = \left[\frac{P}{kT}\cdot\frac{h^3}{(2\pi\cdot 2mkT)^{\frac{3}{2}}}\cdot\frac{\theta_R}{T}(1-e^{-\frac{\theta_V}{T}})\frac{\sigma_{N_2}}{\varepsilon_{N_2}}\right]^{\frac{1}{2}} \left(\frac{T}{\theta}\right)^3 e^{-\frac{[(\Psi_F + \frac{\chi_d}{2}) - \xi(x)(\Psi_F - \Psi_A)]}{kT}}\varepsilon_N = \left(\frac{n}{N-n}\right)_{Fe}\cdot e^{\frac{\xi(x)(\Psi_F - \Psi_A)}{kT}}, \quad (5)$$

where the notation $(n/(N-n))_{x \text{ or } Fe}$ means the value $n/(N-n)$ concerning x-alloy or pure iron respectively.

The general equation for the absorption by pure iron or binary alloys may be expressed by equation (12) in the first report or (5) respectively.

[B] Comparison between Experimental Results and the Equation (5)

The present results given in Figs. 2, 4 and 6 do not represent the isothermal curves rigorously; that is, as were mentioned above, experiments were carried out above 100~150°C over the melting point on Fe-Cr alloys and between 1,400 and 1,600°C on Fe-Mn alloys, though nearly isothermal curve (experimented between 1,600 and 1,650°C) was obtained on Fe-Ni alloys. Since the temperature coefficients are not large compared with the absolute value of saturation, it would be safe to say that the curves shown in Figs. 2, 4 and 6 may be considered as representing nearly isothermal ones. Thus, isothermal relations will hereafter be discussed with respect to equation (5) and Figs. 2, 4 and 6.

In order to check the validity of equation (5), it is convenient to compare the experimental results with equation (5) by taking its logarithms

$$\log\left(\frac{n}{N-n}\right)_x = \log\left(\frac{n}{N-n}\right)_{Fe} + \xi(x)K(T), \quad (6)$$

where $K(T) = (\Psi_F - \Psi_A)/kT$.

* The equation (1) holds only for the statistical distibution of atoms. The rigorous treatment will be perfotmed in the next report.

In Figs. 7, 8 and 9, in which the logarithms of the experimental values of $n/(N-n)$ are plotted against x, the straight line $\overline{AB}$ represents the equation (5) when $\xi(x)=x$, and therefore $\overline{AB}$ corresponds to the case when metal atoms around absorbed nitrogen atoms are in random arrangements (statistically). Nearly such a circumstance is seen in the case of Fe-Mn alloys as shown in Fig. 8. On the other hand, in Fe-Cr and Fe-Ni alloys the experimental curves deviate from straight line $\overline{AB}$ appreciably and are convex upward.

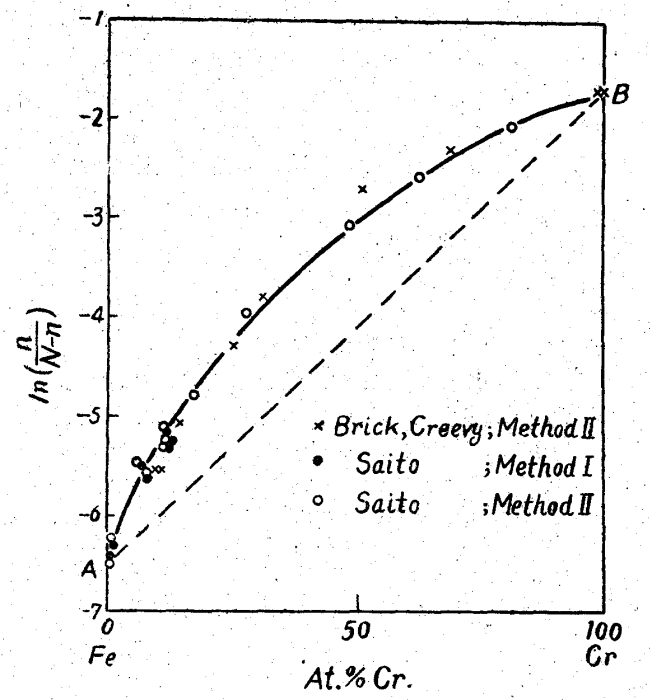

Fig. 7. Examination of the theoretical formula(6) with respect to Fe-Cr alloys.

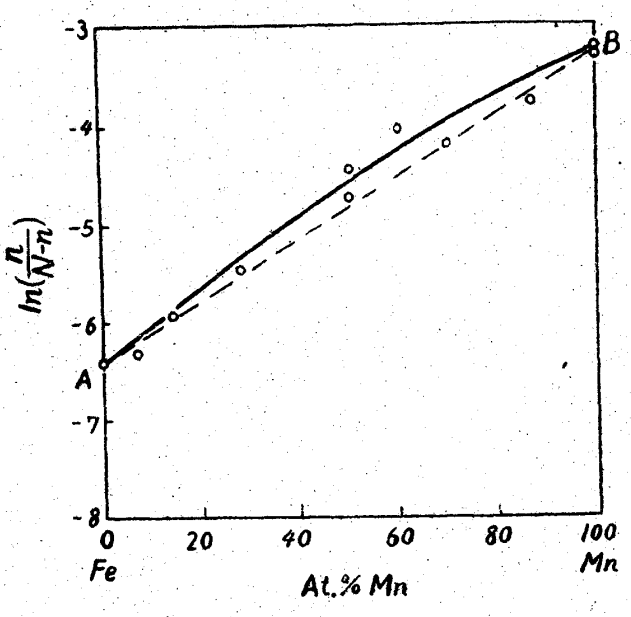

Fig. 8. Examination of the theoretical formula(6) with respect to Fe-Mn alloys.

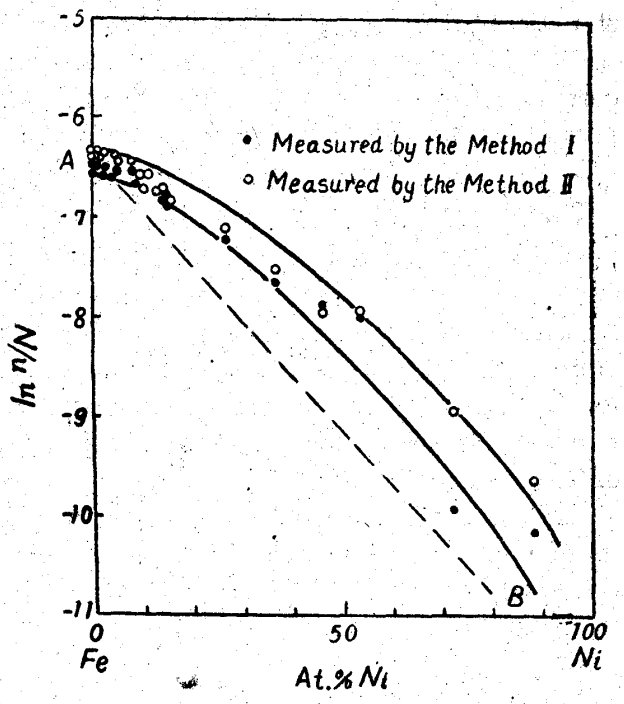

Fig. 9. Examination of the theoretical formula(6) with respect to Fe-Ni alloys.

These facts lead to the following interesting conclusions.

(i) Fe-Cr Alloys

In view of the present result the saturation value of nitrogen by chromium is about 100 times larger than that by iron, it can readily be conceivable that the binding between nitrogen and chromium atom is much stronger than that between nitrogen and iron atoms, i. e., $\Psi_{Cr} > \Psi_F$. Consequently, it is natural to consider that chromium atoms congregate around absorbed nitrogen atoms more than the mean concentration of chromium of the alloy, i. e., $\xi(x) > x$. The convex curve shown in Fig. 7 clearly represents such a fact. In this alloy system, the deviation from the mean concentration line $\overline{AB}$ is considerable.

(ii) Fe-Ni Alloys

On the contrary to the above case, the number of nickel atoms around an absorbed nitrogen atom is smaller than the number zx which corresponds to the mean concentration x of nickel. That is, Fe-atoms congregate more than the mean concentration of Fe of the x-alloy, namely $\xi(x) < x$ as shown in Fig. 9, since nickel has no affinity with nitrogen, i. e., $\Psi_{Ni} \ll \Psi_F$.

(iii) Fe-Mn Alloys

There is no large difference between the interaction energies Ψ_{Mn} and Ψ_F, so that

statistical distribution of atoms around absorbed nitrogen atoms is prevailing in this case, i. e., $\xi(x) \fallingdotseq x$. Consequently, the experimental points plotted in Fig. 8 distribute near the mean concentration line $\overline{AB}$.

The above results can shortly be summarized as follows: the departure of experimental curves AB from the mean concentration line $\overline{AB}$ shows the congregaton of one kind of atom around absorbed nitrogen atoms above its mean concentration, and the amount of deviation is determined by the amount of difference between Ψ_F and Ψ_A.

The conclusion thus obtained from the present experiments will be treated more rigorously in the next report.

Summary

The present results are summarized as follows:

With the increase of additional percentage of chromium or manganese to iron, the saturation values of nitrogen increased from 0.039_1 wt.% N_2 in pure iron (at 1,600°C) up to 4 wt.% N_2 in pure chromium or to 1 wt.% N_2 in pure manganese (at about each melting point). In the case of Fe-Ni alloys, on the contrary, the saturation value decreased with the increase of nickel and the alloys containing over 80% Ni hardly absorbed N_2.

The curves representing the relation between the saturation values and compositions are concave upward as shown in Figs. 2, 4 and 6. These relations could be explained satisfactorily by the theoretical equation (5) or (6) derived from the statistical thermodynamics under the same conception formerly reported.

One of the main conclusions obtained from the comparison between experimental results and theory is as follows: from the standpoint of atomic arrangement, the metal atoms which have large affinity with N-atoms congregate more than the mean concentration of the alloy around absorbed N-atoms; that is, Cr- or Mn-atoms congregate around N-atoms in Fe-Cr or Fe-Mn alloys, and Fe-atoms congregate in Fe-Ni alloys.

References

(1) T. Saitô, Sci. Rep. RITU, A 1 (1949), 411.
(2) M. R. Brick, J. H. Creevy, Metals Tech., 7, No. 3 (1940); Stahl u. Eisen, 60 (1940), 1114; Trans. Am. Inst. Mining Met. Eng., Tech. Pub. No. 1165.